

## Quasicontinuum of metal electronic states and the electronic properties of semiconductor-metal-semiconductor heterostructures

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(Received 29 December 1989)

We present a self-consistent theory of the electronic properties of semiconductor-metal-semiconductor (SMS) heterostructures. This is based upon the method of Green's function within the framework of the tight-binding approximation. The electron dispersion relations are then calculated for a symmetrical SMS system. We discover that the entire electron spectrum presents the character of a two-state system including metal-like states (built-in metal band) and metal-induced semiconductorlike states. We discuss the relevance of this feature to the determination of SMS basic electronic properties.

The recent progress in modern crystal-growth techniques, such as molecular-beam epitaxy, has afforded new possibilities for the preparation of new electronic devices. Because of its careful control of growth conditions, this technique may produce heterostructures with well-defined interfaces. Heterostructure preparation for electronic applications requires, indeed, a high degree of growth control. This is especially true when the heterostructure is formed not only out of different materials belonging to the same family (metals, semiconductors, or insulators) but also combines different families of materials. The semiconductor-metal-semiconductor (SMS) system belongs to this latter kind of heterostructure. In the first case, only chemically different species entering into lattices of different lattice parameters and different crystallography must be matched at interfaces. In the second case, we are also dealing with materials involving different kinds of atomic bonding (e.g., directional bonds in covalent materials). This may add one more degree of difficulty to the interfacial matching problem.

It is now possible to grow such SMS heterostructures with a high degree of interface quality. The most studied structures involve Si and metal silicide layers such as Si/NiSi<sub>2</sub>/Si and Si/CoSi<sub>2</sub>/Si.<sup>1-4</sup> Recently, transistor action has been obtained in this latter system.<sup>2</sup> All these recent advances have motivated active research in this field. Besides these experimental studies, the theoretical investigations on these SMS structures are rather rare. A recent estimation of quantum size effects in thin layered SMS structures has been carried out.<sup>5</sup> In this study, the metal medium is simulated with a free-electron model and isotropic, parabolic energy bands are assumed for both metal and semiconductors with the same effective mass. It is then shown that new quantum-well electronic structures, revealing a two-dimensional electron-gas character, may exist in the metal layer.

In this report, we will present a self-consistent theory of the entire electron structure of SMS heterostructures which may be applied to symmetrical as well as asymmetrical systems. It assumes semi-infinite semiconductor lat-

tics and a finite thickness metal layer. It then allows us to calculate not only the dispersion relations of metal-semiconductor interface states, but also, for a given metal thickness  $L$ , the built-in metal band as well as resonant electronic structures falling within the metal and semiconductor bands. We have discovered that the whole electronic spectrum has the characteristic of a two-state system formed out of related metal-like and metal-induced semiconductorlike states. Each two-state structure will form an electronic doublet and we will discuss the previously mentioned character of each doublet during the presentation of the results.

In what follows, we will briefly present: (i) the main features of metal, semiconductors, and metal-semiconductor interface models used in this microscopic theory and (ii) the formalism. More details will be given in another paper.<sup>6</sup>

We simulate the metal lattice by means of a simple cubic one-band model. The unit lattice mesh has square symmetry within each layer plane. The electronic bulk band, in the nearest-neighbor interaction approximation (hopping integrals  $\gamma_2$ ), is then given by<sup>7</sup>

$$E_2(\mathbf{k}) = E_0 - 2\gamma_2[\cos(ak_x) + \cos(ak_y) + \cos(ak_z)], \quad (1)$$

where  $\mathbf{k}$  is the three-dimensional wave vector,  $E_0$  is the energy level of the band center, and  $a$  is the lattice parameter.

The semiconductor bands are described by using a tight-binding Hamiltonian which accounts only for nearest-neighbor interactions. Sophisticated models use a minimal basis consisting of  $sp^3$ ,  $s^*$  orbitals localized on each lattice site.<sup>8</sup> As we are interested in electronic states falling within the neighborhood of the gap, we may disregard the  $s$ -orbitals on the nonmetallic atoms in the compound (anions), and the  $p$  orbitals on the metallic atoms (cations). This is possible because their associated energies are situated outside the relevant energy domain, contributing slightly to the corresponding electron states. The following relation dispersions are then obtained:

$$E_1 = (E_v + E_c)/2 \pm \left[ (E_v - E_c)^2/4 + 64\gamma_1 \prod_{\sigma=x,y,z} \cos^2(k_\sigma a/2) \right]^{1/2}, \quad (2)$$

where  $k_\sigma$  is the  $\sigma$  component of the wave vector,  $E_r$  and  $E_c$  are orbital self-energies, associated, respectively, with atoms of type 1 (cations) and 2 (anions), and the hopping integral  $\gamma_1$  characterizes the nearest-neighbor interactions.

The SMS structure studied in this article is formed out of a metal layer (thickness  $L$ ) sandwiched between two identical semi-infinite semiconductors. This gives a two-interface system referred to by the integer  $r=1$  or 2. The interfacial crystallography is such that each interface atom (metallic or semiconductor) is surrounded by four nearest-neighbor atoms belonging to the surface of the other (semiconductor or metallic). These semiconductor surfaces may or may not be polar. For our purposes we chose polar surfaces terminated on each metal layer side, respectively, by anions and cations. The whole perturbation induced on separated materials to form the SMS heterostructure may be calculated within the following scheme: (i) create a metallic film and two identical semi-infinite semiconductors terminated by polar surfaces by introducing a partitioned (three components) cleavage operator  $\underline{V}_S$  which will extract these systems from the corresponding bulk materials; (ii) create a SMS structure by introducing interfacial hopping integrals  $\tilde{\gamma}_1$  and  $\tilde{\gamma}_2$  between nearest-neighbor atoms in the metal and semiconductor surfaces (perturbation matrix  $\underline{V}_I$ ). In order to take into account the charge flow across the interfaces, we introduce Coulomb repulsion potentials  $U_{mr}$  and  $U_{scr}$ , respectively, on the metal and semiconductor interface atoms. In fact, this is equivalent to a Hartree-Fock approximation on the Coulomb interaction site. One can limit, as a first approximation, the charge oscillations at each interface to one plane on either interface side. We then obtain for each interface a model with two charged ( $\delta Q_r$  and  $-\delta Q_r$ ) interfacial layers. If we assume the same linear dependence of self-consistent potentials on charge transfer, we obtain by symmetry  $U_{mr} = -U_{scr} = U_r$ . The Fermi level and self-consistent potentials  $U_1$  and  $U_2$  must fulfill the Friedel<sup>9</sup> sum rule, ensuring that the charge neutrality is satisfied,

$$\Delta N(E_F, U_1, U_2) = 0. \quad (3)$$

The numerical calculations are carried out by choosing  $E_F$  and determining for each interface the self-consistent potential in order to satisfy the charge neutrality condition. Once this step has been completed, we proceed to the dispersion relations calculation. The limits and advantages of our model will be discussed in detail elsewhere.<sup>6</sup> One can say that, although this model considers relatively ideal interfaces, it contains all basic elements required to provide a reliable qualitative basis for the studied electronic structure of SMS systems.

In our method, all electronic properties of SMS structure may be calculated once the associated Green's function  $\underline{G}_p$  is known. This may be calculated by using a Dyson-like equation

$$\underline{G}_p = \underline{G}_0 + \underline{G}_0 \underline{D}^{-1} \underline{P}, \quad (4)$$

where  $\underline{G}_0$  represents the matrix of the Green's functions for separated bulk materials. This constitutes a three-block matrix of Green's functions which give the decou-

pled metallic and semiconductor bulk electronic structures. The perturbation-related matrix  $\underline{D}$  is given by the relationship

$$\underline{D} = \underline{I} - \underline{V}_p \underline{G}_0, \quad (5)$$

where the perturbation matrix  $\underline{V}_p$  summarizes all perturbations ( $\underline{V}_S$  and  $\underline{V}_I$ ) induced on the separated materials (when making the heterostructure).  $\underline{I}$  is the unit matrix and  $\underline{D}^{-1}$  the matrix inverse of  $\underline{D}$ . The expression of the elements of  $\underline{D}$  will be given elsewhere.<sup>6</sup> The electronic structure of the SMS system can be determined by resolving the following equation:

$$\det(\underline{D}) = 0. \quad (6)$$

The originality of our method is that we can obtain the dispersion relations of all electronic structures associated with the SMS system, while other standard methods concentrate only on interface states. As we will see, these electronic structures include metal-like states (built-in metal band), semiconductorlike states, and interface states.

In what follows, we will give some results illustrating the main features of SMS symmetrical structures. Figure 1 corresponds to a case in which the bottom of a bulk-

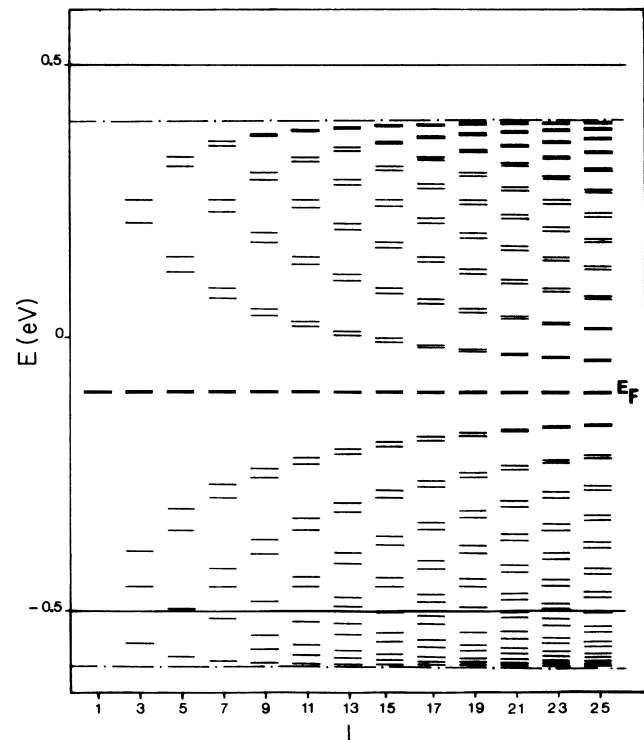


FIG. 1. Energies of two-state electronic structures as a function of metal thickness  $L$  for a symmetrical SMS heterostructure. The limits of the metal bulk band are represented by dash-dotted lines. The valence (lower) and conduction (upper) semiconductor bands are shown as solid lines. The zero of energy is taken at the middle of the semiconductor gap. The chosen example corresponds to  $E_r = E_c = -0.5$  eV,  $\gamma_1 = 1$  eV,  $E_0 = 0.2$  eV,  $\gamma_2 = 0.25$  eV,  $\tilde{\gamma}_1 = \tilde{\gamma}_2 = 0.25$  eV,  $E_F = -0.1$  eV, and  $k_c \cong 0.63 \pi/a$ .

metal band overlaps the upper part of semiconductor valence bands, while the major part of the former band, as well as the metal intrinsic level  $E_0$ , falls within the semiconductor gap. One can clearly see the two-state character of the SMS electronic spectrum. The distance in energy between the two levels of each doublet decreases as the metal thickness  $L$  increases. A first set of levels corresponds to metal-like states, while the second set of levels originates from metal-induced semiconductorlike states, with an interface contribution especially enhanced in the neighborhood of the semiconductor gap. This latter set includes levels localized within the semiconductor gap as well as resonant states falling within the metal and semiconductor bands.

Let us now give some arguments which may establish the previously mentioned characters of these states. Figure 2 represents the dispersion relations of SMS electron

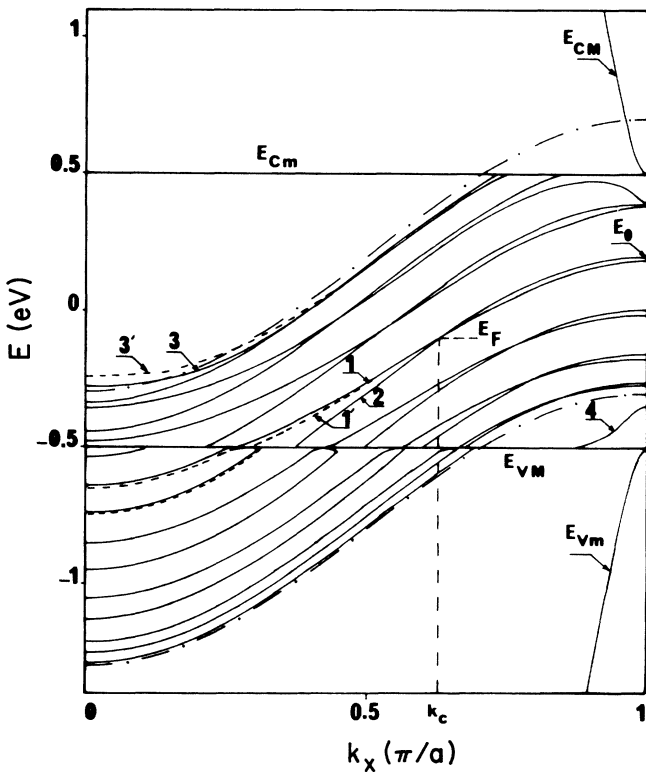


FIG. 2. Electron dispersion relations of an SMS heterostructure along the [100] direction of the interface-Brillouin zone. These reveal the metal electronic signature as two-state systems (e.g., curves 1 and 2). The central two-state structure shows the intersection of its two components at the Fermi level  $E_F$ , for  $k_c \cong 0.63 \pi/a$ . The central metal-like state (curve 2) reaches the metal band center  $E_0$  at the zone boundary.  $E_{cm}$ ,  $E_{cM}$ ,  $E_{cm}$ , and  $E_{cM}$  represent, respectively, the limits of semiconductor valence and conduction bands. The dash-dotted curves represent the bulk-metal band limits. Curve 4 represents an interface state. Curve 3 shows an electronic structure which transforms into an interface state at the long wavelength limit (near the zone center). A nonself-consistent calculation shifts curves 1 and 3 ( $1 \rightarrow 1'$  and  $3 \rightarrow 3'$ ) while the metal-like level (curve 2) remains unchanged. The thickness of the metal layer is  $L=7$ . The remaining parameters are the same as in Fig. 1.

states along the [100] direction of the interface-Brillouin zone. This is the one associated with a heterostructure which keeps the translational periodicity along the direction of the interface plane ( $x,y$ ). The ensuing situation is that the wave-vector component  $k_z$ , perpendicular to the interface plane, is no longer a “good quantum number.” One has to then remove it by standard techniques. This will generate metal and semiconductor bulk bands  $E(k_{\parallel})$  adapted to the interface problem. Strong evidence for the metallic character of the first set is given by analyzing the SMS-associated Bloch waves and their corresponding eigenstates at the bidimensional (interfacial) Brillouin-zone edges. At this short wavelength limit ( $k_x \cong \pi/a$ ), intrinsic features associated with present atomic species may be revealed. Indeed, our results show that the metallic level  $E_0$  is an eigenstate belonging to the first set (Fig. 2, curve 2). Figure 2 also shows the extension of the second set (curve 1) into the semiconductor valence band as resonant doubletlike levels, which may close in near the top of the upper valence band, generally far from metal-like states. This feature has the important consequence that intrinsic metal-like states (built-in metal band) have their energies restricted to the semiconductor gap, ensuring a metallic character to both metal-semiconductor interfaces present in the SMS structure. The upper semiconductorlike state (Fig. 2, curve 3) emerges from the top of the bulk-metal band to give a localized interface state (curve 3'). Curve 4 shows an interface state which emerges from the top of the semiconductor valence band.

The theory presented in this report enables us to discover an important feature which may reveal that the two-

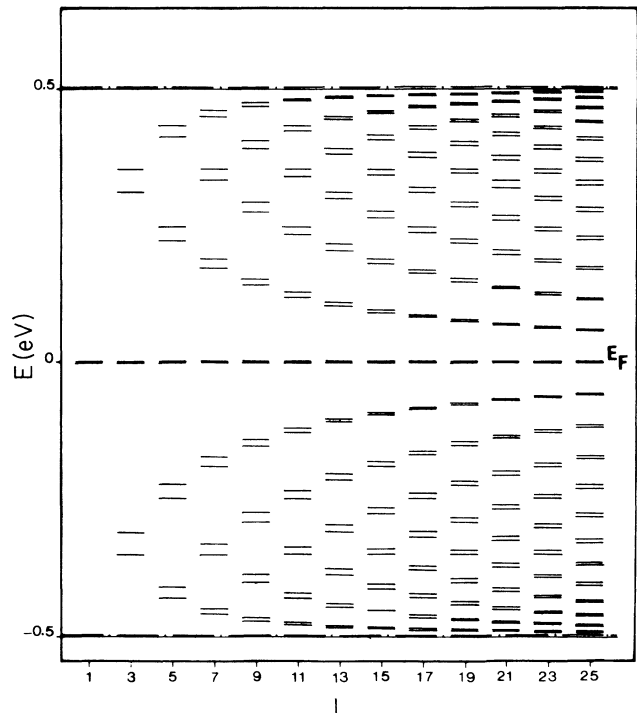


FIG. 3. Same as Fig. 1 with  $E_0=0.2$  eV,  $E_F=0$ , and  $k_c \cong 0.705 \pi/a$ . The remaining parameters are the same as in Fig. 1.

state character of the SMS electronic spectrum plays a basic role in the determination of the fundamental electronic properties of this structure. This feature is shown in Fig. 2. One can notice that the dispersion curves associated with each two-state system intersect one another at a certain value  $k_c$  of the bidimensional wave vector. In the case of Fig. 2, the metal-layer thickness  $L$  is equal to seven, for which seven two-state systems are created. It is worthwhile noting that, among all these two-state structures, the dispersion curve associated with the metal atomic level  $E_0$  (Fig. 2, curve 2) intersects the semiconductorlike level of the doublet (curve 1) at the Fermi level  $E_F$  ( $\cong -0.1$  eV) associated with the heterostructure (for a wave vector  $k_c \cong 0.63 \pi/a$ ). This feature is also represented in Fig. 1 as the pinning of  $E_F$  at this intersection (central doublet). This important result is independent of the choice of parameters, as different sets of parameters reveal the same behavior (Fig. 3).

Let us now emphasize the vital role of self-consistency in our theory. First of all, the semiconductorlike character of metal-induced states (Fig. 2, curve 1) cannot be shown unless we take into account this self-consistency. Indeed, a non-self-consistent approach shifts curve 1 towards curve 1' which, at the short-wavelength limit, reaches the metal-representative level  $E_0$ . Localized interface states are more sensitive to such an effect as shown by the larger energy shift of curve 3 in the neighborhood of that part localized within the semiconductor gap (curve 3  $\rightarrow$  3'). What is more, the interface state corresponding to the short-wavelength limit (curve 4) vanishes in a non-

self-consistent calculation. Such strong sensitivity to interface perturbations is a direct consequence of the interfacial confinement of this latter state.

In conclusion, we have presented a self-consistent microscopic theory of the electronic structure of SMS systems which allows the calculation of the entire SMS electronic spectrum. This shows a two-state character resulting in metal-like states and metal-induced semiconductorlike states which form doublet systems. The two components of each doublet are strongly related, while their basic nature cannot be differentiated unless a self-consistent treatment is carried out. Among all discovered two-state systems, the central doublet system which corresponds to a metal-like state dispersion relation ending at  $E_0$  (metal band center) is of special interest. We have indeed discovered that the Fermi level associated with a SMS structure is pinned at the energy level at which both components of this central doublet intersect. This result is a direct consequence of the charge neutrality condition. Although we have used simple models to describe the metal and semiconductor bulk bands, our theory contains the basic elements required for a reliable qualitative study of such a heterostructure. We hope that this study will stimulate further investigations on such important systems.

The Laboratoire d'Etudes des Surfaces, Interfaces et Composants is "Unité" associée au Centre National de la Recherche Scientifique No. 787.

- <sup>1</sup>E. Rosencher, S. Delage, Y. Campidelli, and F. Arnaud d'Avitaya, *Electron. Lett.* **20**, 762 (1984).  
<sup>2</sup>J. C. Hensel, A. F. J. Levi, R. T. Tung, and J. M. Gibson, *Appl. Phys. Lett.* **47**, 151 (1985).  
<sup>3</sup>E. Rosencher, G. Glastre, G. Vincent, A. Vareille, and F. Arnaud d'Avitaya, *Electron. Lett.* **22**, 699 (1986).  
<sup>4</sup>F. Arnaud d'Avitaya, J. A. Chroboczek, C. d'Anterrosches, G. Glastre, Y. Campidelli, and E. Rosencher, *J. Cryst. Growth*

**81**, 463 (1987).

- <sup>5</sup>M. L. Huberman and J. Maserjian, *Phys. Rev. B* **37**, 9065 (1988).  
<sup>6</sup>P. Masri (unpublished).  
<sup>7</sup>G. Allan, *Ann. Phys. (Paris)* **5**, 169 (1970).  
<sup>8</sup>P. Vogl, H. P. Hjalmarson, and J. D. Dow, *J. Phys. Chem. Solids* **44**, 365 (1983).  
<sup>9</sup>J. Friedel, *Nuovo Cimento, Suppl.* **2**, 287 (1958).